Effect of Molecular Sieves on the Formation and Acid-Catalysed Mono- and Bis-cyclization of *N*-Arylimines: Easy Entry to Polycyclic Ring Systems by a Novel Cascade Reaction

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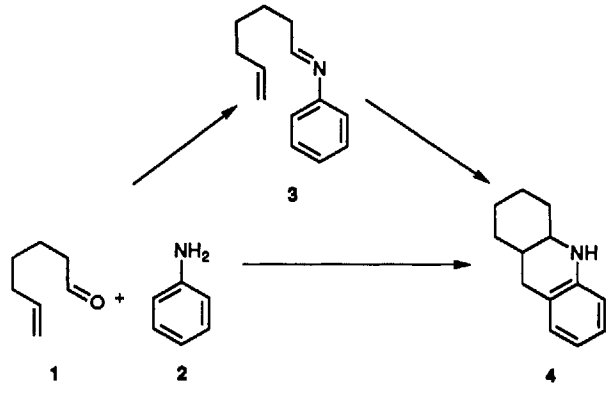
The synthesis of substituted octahydroacridines **14–17** and *N*-arylcyclohexylamines **18–20** from arylamines **5–8** is described. It was found that the isolation of the imines **10–13** and that Lewis acid catalysis could be avoided if molecular sieve beads were used instead of powder. The sequential molecular sieves-catalysed imine-formation/cyclization could be extended to a novel one-pot biscyclization of aryldiamines **29–31** with separated aromatic systems. However, the conversion of aryldiamines **36** and **38** with two amino groups on the same aromatic system into the corresponding biscyclization products **23** and **45** required a two-step procedure under harsher conditions.

The acid-catalysed reaction of *N*-arylimines with alkenes, which can be formally treated as a hetero-Diels–Alder reaction of a 2-azadiene, gives access to various substituted tetrahydroquinolines.[1–9] However, a major drawback in all cyclization and cycloaddition reactions of imines is the necessary activation. This is due to the low electrophilicity of the imine substrate as compared with the corresponding carbonyl compound. The activation of the imine can be achieved in several ways: (a) by electron-withdrawing substituents at the imino nitrogen (*e.g.*, N-Ts, N-acyl),[10,11] (b) by quaternization of the imino nitrogen (*via* iminium ions),[12,13] (c) by electron-withdrawing substituents at the imino carbon (*e.g.*, C-acyl),[11] (d) by enhancing the nucleophilicity of the terminating double or triple bond with a substituent such as OR, SR, NR_2, SiR_3, SnR_3, CH_2SiR_3 or CH_2SnR_3,[14,15] and (e) by Lewis or Brønsted acids (*via* iminium ions).[12] Consequently, an intramolecular cyclization of *N*-arylimines **3**, which are tethered to non-activated alkenes, requires at least activation by a Lewis acid (Scheme 1). We have recently described this reaction in a novel diastereoselective synthesis of substituted octahydroacridine derivatives **4**.[16–18] We found that the cyclization can be carried out very conveniently as a one-pot reaction starting from the α,ω-unsaturated aldehydes **1** and arylamines **2** without isolation of the intermediate imines **3**. If one assumes that the reaction proceeds by a stepwise mechanism *via* cyclization of an iminium ion followed by a subsequent Friedel–Crafts-type cyclization of the tertiary carbenium ion rather than a hetero-Diels–Alder mechanism,[19,20] both steps should be strongly influenced by electronic parameters of the aromatic ring.† Therefore it was interesting to find out how much the one-pot imine-formation/cyclization sequence is dependent on substitutents on the aromatic ring. This investigation eventually should lead to a much milder activation than Lewis acid catalysis. In addition, proper electronic control of the cyclization might allow the introduction and cyclization of a second imino function on the same aromatic ring. If both diimine formation and biscyclization could be obtained in one sequential transformation, this would be a highly desirable method for the preparation of aza-polycyclic systems, in which isolation and purification of intermediates could be avoided as much as possible.[21–23] We here report on a novel catalysis of arylimino cyclizations by molecular sieves and a novel tandem bisimine formation/biscyclization reaction giving rise to aza-polycyclic systems.

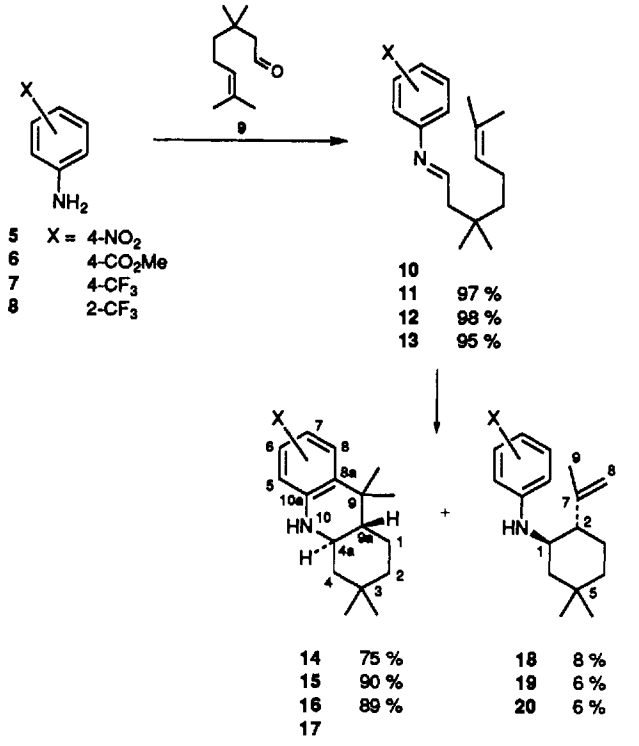


Scheme 1

Results and Discussion

According to our previous investigations on Lewis acid-catalysed cyclizations of *N*-arylimines and η^6-(iminoarene)chromium complexes,[16,17] it seemed reasonable that electron-withdrawing substituentes on the aromatic ring should favour the cyclization most, because the electrophilicity of the imine is increased. Therefore the *para*- and *ortho*-substituted anilines **5–8** were treated with 3-methylcitronellal **9** in the presence of molecular sieves 4 Å and the conversion was monitored by NMR spectroscopy and analytical high-performance liquid chromatography (HPLC) (Scheme 2). It turned out that the reaction was strongly dependent on the type of molecular sieve used. When *powdered* molecular sieves were used, the anilines **6–8** gave very pure imines **11–13** in almost quantitative yield after 15 min. 4-Nitroaniline **5**, however, could not be converted into the desired imine **10**. On the other hand, reaction of compound **5** in the presence of molecular sieve *beads* resulted in the formation of a mixture of the *trans*-configurated cyclization product **14** together with monocyclization product **18** as a by-product (**14**:**18** 94.1:5.9). After separation by flash chromatography, compounds **14** and **18** were isolated in 75 and 8% yield, respectively. The occurrence of compound **18** can be reationalized by a hetero-ene reaction of *N*-arylimine **10**.

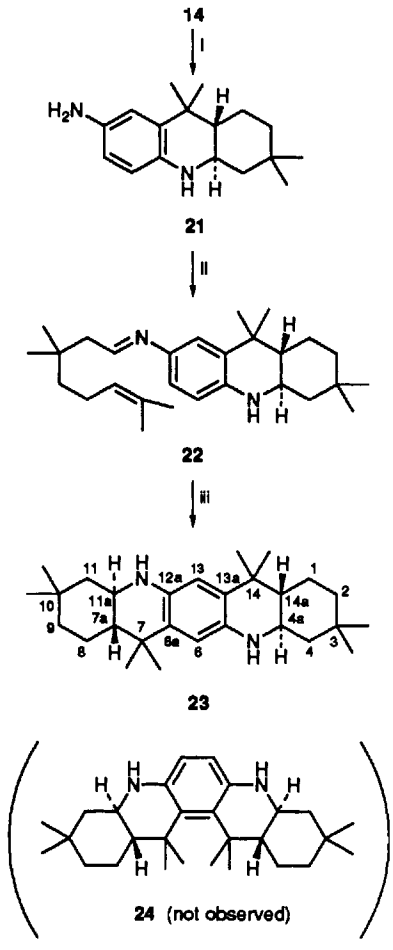
† According to semi-empirical calculations by Tietze *et al.*, reactions of 2-azadienes with dienophiles follow a stepwise mechanism, whereas the corresponding 2-oxabutadienes react through a Diels–Alder-type mechanism (see ref. 20). We would like to thank Prof. Tietze for informing us of his calculations on 2-azabutadienes prior to publication.



Scheme 2 *Reagents and conditions:* Molecular sieves 4 Å, CH_2Cl_2, 25 °C, 1 day

Despite various known Lewis acid-catalysed hetero-ene reactions of *N*-benzylimines,[24–26] there is no precedent for the analogous *N*-arylimines in the literature. The formation of the hetero-ene product in these Lewis-catalysed cyclizations was rather unexpected because, in our earlier studies with (*o*-toluidine)chromium tricarbonyl,[17] the corresponding hetero-ene products were never observed, although the chromium tricarbonyl fragment is supposed to activate the aromatic ring comparable to the effect of one nitro group. When methyl *p*-aminobenzoate **6** was treated with molecular sieve *beads*, the cyclization product **15** and the ene product **19** were obtained (**14**:**19** 94.8:5.2; for isolated yields see Experimental section). Under similar conditions *p*-(trifluoromethyl)aniline **7** gave the products **16** and **20** (**16**:**20** 88.5:11.5). In contrast, *o*-(trifluoromethyl)aniline **8** gave a mixture of the imine **13** and only a small amount of cyclization product **17** (**13**:**17** 74.0:26.0) under the same conditions. The low tendency of imine **13** to cyclize might be due to the steric hindrance of the *ortho*-substituent. The *trans*-configuration of the hetero-ene products **18**–**20** was deduced from the vicinal coupling constants of 1-H in their ^{1}H NMR spectra (*e.g.*, for compound **18**: ddd, $J_{1,2}$ 10.6 Hz, $J_{1,6ax}$ 10.4 Hz, $J_{1,6eq}$ 3.8 Hz).[27,*]

We were especially interested in the nitro-substituted cyclization product **14**, because the remaining nitro group might allow us to perform a second cyclization *via* reduction/imine-formation sequence in the same aromatic system. In order to test this hypothesis, compound **14** was reduced with Raney-Ni/hydrazine[28] to give the amine **21** in quantitative yield (Scheme 3). The amine **21** was then converted into the imine **22** in the presence of *powdered* molecular sieves and the final cyclization was achieved by treatment of imine **22** with 2 mol equiv. of $MeAlCl_2$. As expected from our earlier investigations,[16] ^{1}H NMR spectra indicated exclusive formation of the *trans*-ring fusion



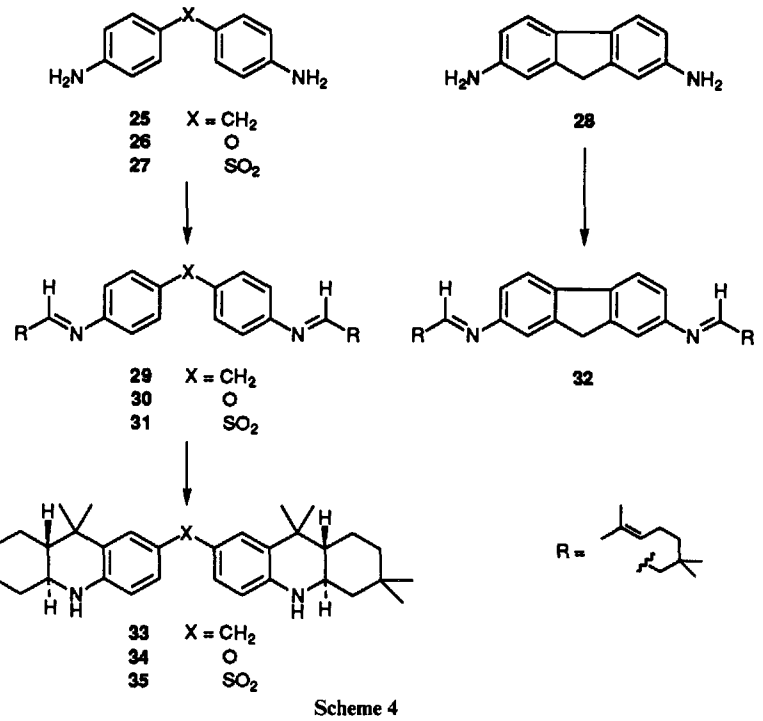
Scheme 3 *Reagents and conditions:* i, Ra-Ni, H_2NNH_2, EtOH, reflux, 30 min (99%); ii, **9**, mol sieves 4 Å (powder), CH_2Cl_2, 25 °C (99%); iii, $MeAlCl_2$ (2.5 mol equiv.), CH_2Cl_2, −78 °C, then 25 °C, 2 days (94%)

production. Out of the two possible regioisomers, the C_2-symmetrical product **23** and the C_s-symmetrical product **24**, only the sterically less hindered compound **23** was observed.† Therefore, the second cyclization proceeded with complete regio- and stereo-selectivity. The remarkable stability of compound **23** could be deduced from its characteristic low-resolution mass spectrum (EI), which showed only three major peaks, *i.e.* *m*/*z* 408 (M^+, 100%), 391 (84) and 69 (55). All other fragments in the mass spectrum showed intensities below 26%.

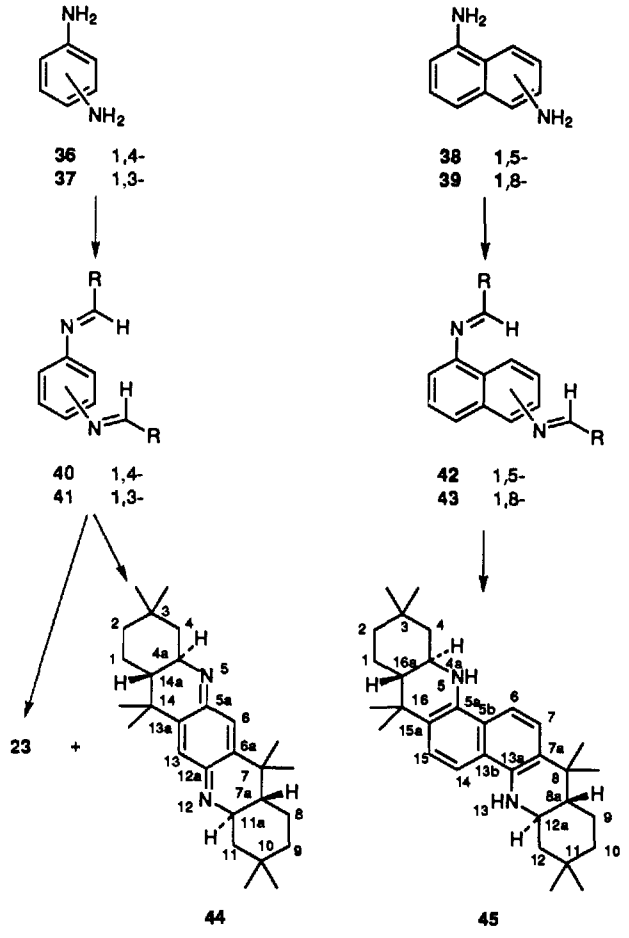
In order to develop a more direct approach to biscyclization products (*e.g.*, **23**), the conversion of aryldiamines **25**–**28** and **36**–**39** into the corresponding diimines and their cyclization was envisaged (Schemes 4, 5). First, diphenylmethyl derivatives/analogues **25**–**27** were used, so that possible electronic interactions between the two imino groups during imine formation and cyclization could be either minimized or counterbalanced by the tether. The results which were obtained for the cyclization of 4-nitroaniline **5** could be transferred to the diphenyl compound **25**. Monitoring of the reaction between, 4,4′-diaminodiphenylmethane **25** and 2 mol equiv. of 3-methylcitronellal **9** in the

* For the determination of *cis*/*trans*-configurations of octahydroacridines by NMR spectroscopy see ref. 16. See also ref. 27.

† The relative configuration (4a*RS*,7a*SR*,11a*RS*,14a*SR*) of compound **23** and related biscyclization products was deduced from the fact that only one signal for 7a-H/14a-H, and one signal for 4a-H/11a-H, was observed in the ^{1}H NMR spectrum. For another possible diastereoisomer with (4a*RS*,7a*RS*,11a*SR*,14a*SR*) configuration one would expect four signals, *i.e.* for 7a-H, 14a-H, 4a-H and 11a-H. We do not have any explanation for the exclusive formation of compound **23**.



Scheme 4



Scheme 5

presence of molecular sieve *beads* at room temperature by NMR spectroscopy indicated a rapid formation of the diimine **29**, which was complete after 15 min. After 3 h both the characteristic pseudo-triplet at 5.17 (HC=C<) and signals of the biscyclization product **33** could be observed in the ^{1}H NMR spectrum. After 24 h the biscyclization was complete as determined by NMR spectroscopy and compound **33** was isolated in 57% yield. Treatment of compound **25** with aldehyde **9** in the presence of *powdered* molecular sieves gave, as expected, complete formation of the diimine **29** after 15 min with no further cyclization. Therefore diimine **29** was isolated, and treated with $MeAlCl_2$ to yield the biscyclization product **33** (67%). The one-pot biscyclization worked equally well for both electron-donating and -withdrawing groups X in the tether. Thus, the biscyclization product **34** with an oxygen tether was isolated in 68% yield, while compound **35** with a sulfone bridge was obtained in 58% yield.* Although the diimine **32** of fluorene-2,7-diamine **28** could be prepared in an analogous way, any attempted biscyclization resulted in decomposition of the starting material.

Next, aromatic diamines **36–39** having two amino groups on the same aromatic system were tested. While both *para*- and *meta*-disubstituted phenylenediamines **36**, **37** could be converted into the corresponding diimines **40** and **41**, only the *para*-disubstituted diimine **40** cyclized further in the presence of Lewis acid. However, this particular diimine confronted us with a surprising result. Treatment of compound **40** with 2.5 mol equiv. of $MeAlCl_2$ gave a mixture of the expected *trans*-biscyclization product **23** together with the novel quinone diimine **44** (**23**:**44** 52.6:47.4). Both compounds could be separated by preparative HPLC.† In contrast to the numerous quinone diimines with electron-withdrawing substituents at the C=N group (*e.g.*, CO_2R, CN, SO_2R),[29] there were only two isolable *N*-alkylquinone diimines previously known, namely the *N*,*N*′-dimethyl and the *N*,*N*′-dicyclohexyl derivatives.[30,31] This is probably due to their reported instability,[29–32] especially in the presence of acids. Although we do not know whether the quinone diimine **44** is formed as an intermediate during the cyclization sequence or afterwards by an oxidation of diamine

* All attempts to prepare the sulfonyl diimine **31** by the powdered molecular sieves method failed.

† The structure of quinone diimine **44** was supported by an X-ray crystal-structure determination. However, the *R*-values were insufficient for publication (R = 0.086, R_w^2 = 0.281), so that further details of the structure will not be discussed here.

23, the presence of compound **44** in a Lewis acidic environment gave some evidence for its stability.

Different behaviour of *meta*- and *para*-disubstituted systems was also observed in the case of naphthalenediamines **38**, **39**. While the 1,5-disubstituted naphthalenediamine **38** reacted cleanly to give the diimine **42**, which could be further converted into the biscyclization product **45** in the presence of $MeAlCl_2$, the diimine **43** of the corresponding 1,8-disubstituted substrate **39** could not be obtained under these conditions. Several conclusions can be drawn from these results: although the diimino compounds of those diamines with two amino functions on the same aromatic system were accessible by using *powdered* molecular sieves, it was not possible to convert the diimines in a single step into the biscyclization products by using molecular sieve *beads*. That means that the presence of a second imino function decreases the reactivity of the first, so that stronger activation, *e.g.* by Lewis acids, is required in order to obtain the biscyclization products. However, this novel cascade reaction (*i.e.*, the sequential molecular sieves-catalysed diimine-formation/biscyclization method) can be used very successfully for diamines with 'separated' aromatic systems. The second conclusion was that the two amino functions should be positioned as far away from each other as possible, so that no unfavourable steric interactions are possible. The different reactivity of molecular sieve *beads* and *powder* in the cyclization might be explained in the following way. Molecular sieves of the zeolite A-type are aluminosilicates with an Al/Si ratio of 1:1 and Na^+/K^+ as counterions in the negatively charged framework.[33-35] Therefore the zeolite can be considered either as a cation exchanger (*i.e.*, it traps acid from the solution) or a Brønsted acid (which can be dehydroxylated to a Lewis acid by high temperature) and the catalytic activity depends on whether the acid-trapping or the Brønsted acidic[34] properties outweigh the other. *Powdered* molecular sieves seem to be much more efficient in acid trapping, because of their increased surface as compared with that of *beads*. If one assumes that formation of imine requires only catalytic amounts of acid, the trace amounts in *powdered* sieves should be sufficient to catalyse the reaction. In contrast, the cyclization requires stronger acidic conditions, because the product amines are more basic than the starting imines, so that the product competes with starting material for the acid catalyst. Thus *beads* are needed for successful cyclization. Despite its limitations to activated arylamines, the novel molecular sieves-catalysed cascade reaction has several advantages over Lewis acid-catalysed processes: (1) the reaction conditions are much milder, (2) no low-temperature equipment is necessary, (3) the work-up procedure is very easy and convenient.

Experimental

General.—All cyclizations were carried out under argon, using standard Schlenk techniques. Solvents were dried and deoxygenated by standard procedures. Analytical TLC was performed on precoated Merck SiO_2 254 F plates (0.25 mm thickness) and compounds were visualized with a solution of phosphomolybdic acid in EtOH (5%, v/v). Flash chromatograhy was carried out with silica gel 60 (230–400 mesh). M.p.s were measured on a Gallenkamp apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were run on a Bruker AM 200 spectrometer at 200 and 50 MHz respectively. IR spectra were recorded on a DIGILAB FTS-45 FT-IR spectrometer by diffuse reflection. Mass spectra were obtained at an ionization potential of 70 eV. 3,3,7-Trimethyloct-6-enal **9** was prepared according to ref. 36. Analytical HPLC was carried out with a JASCO PU-980 gradient pump and a JASCO 875-UV detector at 300 nm coupled with a Shimadzu C-R6A Chromatopac integrator. Preparative HPLC was carried out on a Knauer Compact HPLC with a Knauer variable-wavelength detector at 300 nm. The following conditions were used for HPLC—*Analytical:* JASCO Si 100 5μ column, 250 × 4.6 mm, flow 1.0 $cm^3\ min^{-1}$, eluent hexanes–ethyl acetate (99:1) (monocyclizations) or hexanes–ethyl acetate–triethylamine (98:1:1) (biscyclizations). *Preparative:* JASCO Si 100 10μ column, 250 × 25 mm, flow 30 $cm^3\ min^{-1}$, eluent n-hexane–ethyl acetate–triethylamine (98:1:1). Light petroleum refers to the fraction with distillation range 45–65 °C

General Procedure for the Preparation of Monoimines **11–13**, **22** *and Diimines* **29–32**, **40–42**.—To a solution of monoamine (1.00 mmol) or diamine (0.50 mmol) and 3-methylcitronellal **9** (168 mg, 1.00 mmol) in dichloromethane (4.5 cm^3) in a screw-cap bottle (5 cm^3) was added powdered molecular sieves 4 Å and the mixture was stirred at room temperature. After complete conversion, the mixture was filtered and evaporated to yield the imines as analytically pure compounds.

Methyl 4-(3′,3′,7′-*trimethyloct*-6′-*enylideneamino*)*benzoate* **11**. *Oil* (291 mg, 97%); ν_{max}(KBr)/cm^{-1} 1711 (C=O, ester), 1653 (C=N), 1605, 1517 (C=C) and 1277 (C–O); δ_H(200 MHz; C_6D_6) 0.88 (6 H, s, 10′- and 11′-H_3), 1.20 (2 H, m, 4′-H_2), 1.49 and 1.62 (6 H, s, 8′- and 9′-H_3), 1.90 (2 H, m, 5′-H_2), 2.20 (2 H, d, *J* 5.7, 2′-H_2), 3.56 (3 H, s, CO_2Me), 5.10 (1 H, m, 6′-H), 6.88 (2 H, d, *J* 6.7, 3- and 5-H), 7.60 (1 H, t, *J* 5.7, 1′-H) and 8.02 (2 H, t, *J* 6.7, 2- and 6-H); δ_C(50 MHz; C_6D_6) 17.6, 23.1, 25.8, 27.5, 34.1, 42.8 and 48.1 (C-2′, -3′, -4′, -5′, -8′, -9′, -10′ and -11′), 120.9 (C-6′), 112.3, 113.7, 131.1 and 132.1 (C-2, -3, -5, -6 and -7′), 147.8 (C-1), 157.2 (C-4), 166.3 (C-1′) and 167.0 (CO_2Me) (Found: M^+, 301.2037. $C_{19}H_{27}NO_2$ requires M, 301.2042).

4-(*Trifluoromethyl*)-N-(3′,3′,7′-*trimethyloct*-6′-*enylidene*)*aniline* **12**. *Oil* (305 mg, 98%); ν_{max}(KBr)/cm^{-1} 1652 (C=N), 1614, 1530 (C=C), 1321, 1120 (C–F) and 827 (1,4-disubstituted aryl); δ_H(200 MHz; C_6D_6) 0.87 (6 H, s, 10′- and 11′-H_3), 1.20–1.29 (2 H, m, 4′-H_2), 1.56 and 1.67 (6 H, s, 8′- and 9′-H_3), 1.98 (2 H, m, 5′-H_2), 2.20 (2 H, d, *J* 5.6, 2′-H_2), 5.13 (1 H, m, 6′H), 6.76 (2 H, d, *J* 8.5, 2- and 6-H), 7.33 (2 H, d, *J* 8.5, 3- and 5-H) and 7.53 (1 H, t, *J* 5.6, 1′-H); δ_C(50 MHz; C_6D_6) 17.6, 23.1, 25.8, 27.5, 34.1, 42.8 and 48.1 (C-2′, -3′, -4′, -5′, -8′, -9′, -10′ and -11′), 120.9 (C-6′), 112.3, 114.0, 125.2, 126.4 and 156.1 (C-1, -2, -3, -4, -5, -6 and CF_3), 131.1 (C-7′) and 166.3 (C-1′); *m*/*z* 311 (M^+, 35%), 296 (M − CH_3, 34), 292 (M − F, 34), 215 (68), 187 (64), 109 (72), 69 (100) and 55 (70) (Found: M^+, 311.1860. $C_{18}H_{24}F_3N$ requires M, 311.1852).

2-(*Trifluoromethyl*)-N-(3′,3′,7′-*trimethyloct*-6′-*enylidene*)*aniline* **13**. *Oil* (295 mg, 95%); ν_{max}(KBr)/cm^{-1} 1657 (C=N), 1602 and 1582 (C=C), 1319, 1112 (C–F) and 760 (1,2-disubstituted aryl); δ_H(200 MHz; C_6D_6) 0.87 (6 H, s, 10′- and 11′-H_3), 1.21–1.29 (2 H, m, 4′-H_2), 1.54 and 1.65 (6 H, s, 8′- and 9′-H_3), 1.96 (2 H, m, 5′-H_2), 2.20 (2 H, d, *J* 5.6, 2′-H_2), 5.14 (1 H, m, 6′-H), 6.49 (1 H, d, *J* 7.6, 6-H), 6.78 and 7.03 (2 H, t, *J* 7.5, 4- and 5-H), 7.44 (1 H, d, *J* 7.5, 3-H) and 7.53 (1 H, t, *J* 5.6, 1′-H); δ_C(50 MHz; C_6D_6) 17.6, 23.1, 25.8, 27.4, 34.1, 42.9 and 48.4 (C-2′, -3′, -4′, -5′, -8′, -9′, -10′ and -11′), 120.3 (C-6′), 124.6, 125.2, 126.1, 126.2, 126.3, 132.9 and 152.1 (C-1, -2, -3, -4, -5, -6 and CF_3), 130.9 (C-7′) and 166.7 (C-1); *m*/*z* 311 (M^+, 15%), 296 (M^+ − CH_3, 16), 292 (M^+ − F, 8), 228 (100), 215 (69), 187 (81), 69 (86) and 57 (83) (Found: M^+, 311.1861).

trans-3,3,9,9-*Tetramethyl*-(3′,3′,7′-*trimethyl*-6′-*oct*-6′-*enylideneamino*)-1,2,3,4,4a,9,9a,10a-*octahydroacridine* **22**. *Brown oil* (404 mg, 99%; ν_{max}(KBr)/cm^{-1} 1677 and 1671 (C=C, C=N), 1612, 1551 and 1509 (C=C) and 810 (1,3,4-trisubstituted aryl); δ_H(200 MHz; C_6D_6) 0.81 and 0.88 (6 H, s, 10′- and 11′-H_3), 0.90 (6 H, s, 3-Me_2), 1.07 and 1.24 (6 H, s, 9-Me_2), 1.59 and 1.66 (6 H, s, 8′- and 9′-H_3), 0.80–1.80 (9 H, m, 1-, 2-, 4- and 4′-H_2 and 9a-H), 2.03–2.13 (2 H, m, 5′-H_2), 2.37 (2 H, d, *J* 5.6, 2′-H_2), 2.86–3.15 (2 H, m, NH and 4a-H), 5.18 (1 H, m, 6′-H), 6.29 (1 H, d, *J* 8.4, 5-H), 7.01 (1 H, dd, *J* 8.4 and 2.3, 6-H), 7.40 (1 H,

d, *J* 2.3, 8-H) and 8.01 (1 H, t, *J* 5.6, 1'-H); δ_C(50 MHz; C_6D_6) 17.7, 21.1, 23.2, 25.2, 25.9, 26.9, 27.4, 27.7, 30.8, 33.2, 34.1, 35.1, 39.4, 42.9, 47.4, 48.0 and 48.3 (C-1, -2, -3, -4, -4a, -9, 9a, 3-Me_2, 9-Me_2, -2', -3', -4', -5', -8', -9', -10' and -11'), 114.6, 118.7, 121.0, 125.6, 130.7, 132.0, 142.4 and 143.1 (C-5, -6, -7, -8, -8a, -10a, -6' and -7') and 158.7 (C-1'); *m/z* 408 (M^+, 79%), 284 (70), 71 (85), 69 (100) and 55 (92) (Found: M^+, 408.3504. $C_{28}H_{44}N_2$ requires M, 408.3495).

Bis[4-(3',3',7'-*trimethyloct*-6'-*enylideneamino*)*phenyl*]*methane* **29**. *Yellow oil* (237 mg, 95%); ν_{max}(KBr)/cm^{-1} 1648 (C=N), 1615 and 1505 (C=C); δ_H(200 MHz; C_6D_6) 0.84 (12 H, s, 10'- and 11'-H_3), 1.11 (4 H, m, 4'-H_2), 1.41 and 1.47 (12 H, s, 8'- and 9'H_3), 1.84 (4 H, m, 5'-H_2), 2.13 (4 H, d, *J* 5.6, 2'-H_2), 3.71 (2 H, s, CH_2), 4.92 (2 H, m, 6'-H), 6.71 (2 H, dd, *J* 8.4 and 3.5, 2- and 6-H), 6.91 (2 H, dd, *J* 8.4 and 4.2, 3- and 5-H) and 7.69 (2 H, t, *J* 5.6, 1'-H); δ_C(50 MHz; C_6D_6) 17.7, 21.8, 25.8, 33.5, 43.4 and 48.0 (C-2', -3', -4', -5', -8', -9', -10' and -11'), 121.2 (C-6'), 125.7 and 129.9 (C-2, -3, -5, -6), 131.3 (C-7'), 139.2 (C-4), 151.9 (C-1) and 164.2 (C-1'); *m/z* 498 (M^+, 58%), 484 (51), 483 (M^+ − CH_3, 44), 252 (75), 106 (100), 71 (78), 69 (92) and 55 (75) (Found: M^+, 498.3973. $C_{35}H_{50}N_2$ requires M, 498.3974).

Bis[4-(3',3',7'-*trimethyloct*-6'-*enylideneamino*)*phenyl*] *ether* **30**. *Yellow oil* (238 mg, 95%); ν_{max}(KBr)/cm^{-1} 1644 (C=N), 1598 and 1511 (C=C) and 840 (1,4-disubstituted aryl); δ_H(200 MHz; C_6D_6) 0.90 (12 H, s, 10'- and 11'-H_3), 1.26 (4 H, m, 4'-H_2), 1.56 and 1.66 (12 H, d, 8'- and 9'-H_3), 2.00 (4 H, m, 5'-H_2), 2.27 (4 H, d, *J* 5.6, 2'-H_2), 5.15 (2 H, m, 6'-H), 6.91–7.02 (8 H, m, 2-, 3-, 5- and 6-H) and 7.75 (2 H, t, *J* 5.6, 1'-H); δ_C(50 MHz; C_6D_6) 17.6, 23.1, 25.8, 27.6, 34.1, 42.8 and 48.1 (C-2', -3', -4', -5', -8', -9', -10' and -11'), 119.7 (C-6'), 122.3 and 125.3 (C-2, -3, -5 and -6), 130.9 (C-7'), 148.7 (C-4), 155.9 (C-1) and 163.5 (C-1'); *m/z* 500 (M^+, 57%), 417 (50), 350 (59), 254 (64), 109 (84), 108 (95), 70 (90) and 55 (100) (Found: M^+, 500.3766. $C_{34}H_{48}N_2O$ requires M, 500.3751).

2,7-*Bis*(3',3',-7'-*trimethyloct*-6'-*enylideneamino*)*fluorene* **32**. *Brown oil* (243 mg, 98%); ν_{max}(KBr)/cm^{-1} 1644 (C=N), 1615, 1585 and 1514 (C=C) and 855 and 817; δ_H(200 MHz; C_6D_6) 0.94 (12 H, s, 10'- and 11'-H_3), 1.33 (4 H, m, 4'-H_2), 1.49 and 1.57 (12 H, s, 8'- and 9'-H_3), 2.03 (4 H, m, 5'-H_2), 2.33 (4 H, d, *J* 5.6, 2'-H_2), 3.54 (2 H, s, 9-H_2), 5.16 (2 H, m, 6'-H), 7.12 (2 H, d, *J* 1.9, 1- and 8-H), 7.17 (2 H, dd, *J* 7.9 and 1.9, 3- and 6-H), 7.56 (2 H, d, *J* 7.9, 4- and 5-H) and 7.85 (2 H, t, *J* 5.6, 1'-H); δ_C(50 MHz; C_6D_6) 17.7, 23.2, 25.8, 27.6, 34.1, 37.0, 43.0 and 48.3 (C-9, -2', -3', -4', -5', -8', -9', -10' and -11'), 120.2 (C-6'), 117.7, 120.3 and 125.4 (C-1, -3, -4, -5, -6 and -8), 131.0 (C-7'), 139.5 and 144.7 (C-4a, -4b, -8a and -9a), 152.1 (C-2 and -7) and 163.5 (C-1'); *m/z* 496 (M^+, 100%), 478 (38), 413 (50), 248 (50), 149 (59), 123 (52), 83 (56), 69 (70) and 55 (58) (Found: M^+, 496.3817. $C_{35}H_{48}N_2$ requires M, 496.3806).

N,N'-*Bis*(3',3',7'-*trimethyloct*-6'-*enylidene*)-p-*phenylenediamine* **40**. *Pale yellow oil* (200 mg, 98%); ν_{max}(KBr)/cm^{-1} 1647 (C=N), 1582 and 1505 (C=C) and 784 (1,4-disubstituted aryl); δ_H(200 MHz; C_6D_6) 0.91 (12 H, s, 10'- and 11'-H_3), 1.25 (4 H, m, 4'-H_2), 1.56 (6 H, s, 9'-H_3), 1.66 (6 H, s, 8'-H_3), 2.00 (4 H, m, 5'-H_2), 2.27 (4 H, d, *J* 5.6, 2'-H_2), 5.15 (2 H, m, 6'-H), 7.04 (4 H, s, 2-, 3- 5- and 6-H) and 7.76 (2 H, t, *J* 5.6, 1'-H); δ_C(50 MHz; C_6D_6) 17.7, 23.2, 25.9, 27.6 and 34.1 (C-3', -4', -8', -9', -10' and -11'), 42.8 (C-5'), 48.2 (C-2'), 121.7 (C-6'), 125.4 (C-2, -3, -5 and -6), 130.9 (C-7'), 150.8 (C-1 and -4) and 163.6 (C-1'); *m/z* 408 (M^+, 62%), 393 (M^+ − CH_3, 42), 69 (100) and 57 ($C_4H_9^+$, 82) (Found: M^+, 408.3504. $C_{28}H_{44}N_2$ requires M, 408.3495).

N,N'-*Bis*(3',3',7'-*trimethyloct*-6'-*enylidene*)-1,3-*phenylenediamine* **41**. *Yellow oil* (194 mg, 98%); ν_{max}(KBr)/cm^{-1} 1648 (C=N), 1595 and 1510 (C=C) and 772 (1,3-disubstituted aryl); δ_H(200 MHz; C_6D_6) 0.88 (12 H, s, 10'- and 11'-H_3), 1.267 (4 H, m, 4'-H_2), 1.56 and 1.66 (12 H, s, 8'- and 9'-H_3), 1.98 (4 H, m, 5'-H_2), 2.24 (4 H, d, *J* 5.6, 2'-H_2), 5.14 (2 H, m, 6'-H), 6.90 (2 H, dd, *J* 7.2 and 1.7, 4- and 6-H), 6.99 (1 H, d, *J* 1.7, 2-H), 7.14 (1 H, d, *J* 7.2, 5-H) and 7.76 (2 H, t, *J* 5.6, 1'-H); δ_C(50 MHz; C_6D_6) 17.7, 23.1, 25.8, 27.6, 34.0, 42.8 and 48.1 (C-2', -3', -4', -5', -8', -9', -10' and -11'), 117.8 (C-6'), 113.4, 120.2, 125.3, 125.4 and 129.8 (C-2, -4, - 5 and -6), 130.9 (C-7'), 154.4 (C-1 and -3) and 164.5 (C-1'); *m/z* 408 (M^+, 15%), 393 (M^+ − CH_3, 12), 365 (14), 175 (52), 134 (53), 108 (72), 69 (100) and 55 (72) (Found: M^+, 408.3504).

N,N'-*Bis*(3',3',7'-*trimethyloct*-6'-*enylidene*)*naphthalene*-1,5-*diamine* **42**. *Brown amorphous solid* (218 mg, 95%); ν_{max}(KBr)/cm^{-1} 1647 (C=N), 1615, 1515, 1505 (C=C) and 828; δ_H(200 MHz; C_6D_6) 0.94 (12 H, s, 10'- and 11'-H_3), 1.34 (4 H, m, 4'-H_2), 1.64 and 1.68 (12 H, s, 8'- and 9'-H_3), 2.20 (4 H, m, 5'-H_2), 2.35 (4 H, d, *J* 5.6, 2'-H_2), 5.17 (2 H, m, 6'-H), 6.77 (2 H, d, *J* 7.1, 4- and 8-H), 7.34 (2 H, dd, *J* 8.6 and 7.1, 3- and 7-H), 7.79 (2 H, t, *J* 5.6, 1'-H) and 8.39 (2 H, d, *J* 8.6, 2- and 6-HG); δ_C(50 MHz; C_6D_6) 17.7, 23.2, 25.9, 27.6, 34.1, 42.9 and 48.3 (C-2, -3', -4', -5', -8', -9', -10' and -11'), 121.9 (C-6'), 113.8, 125.4, 126.1 and 129.5 (C-2, -3, -4, -6, -7, -8, -9 and -10), 130.9 (C-7'), 150.5 (C-1 and -5) and 164.8 (C-1'); *m/z* 458 (M^+, 45%), 456 (34), 225 (48), 169 (50), 69 (100) and 55 (52) (Found: M^+, 458.3661. $C_{32}H_{46}N_2$ requires M, 458,3676).

General Procedure for the Sequential Imine Formation/Cyclization.—To a solution of 3-methylcitronellal **9** (840 mg, 5 mmol) and an aryl monoamine (5 mmol) or aryl diamine (2.5 mmol) in dichloromethane (50 cm^3) were added molecular sieve beads (4 Å; 2 g) and the mixture was stirred for 2 days at room temperature. After filtration and evaporation of the mixture the crude product was purified by flash chromatography on silica gel [light petroleum–ethyl acetate (15:1)] to yield octahydroacridines as the major products and ene products as minor products. In the case of biscyclizations no ene products were observed.

trans-3,3,9,9-*Tetramethyl*-7-*nitro*-1,2,3,4,4a,9,9a,10-*octahydroacridine* **14**. *Deep yellow crystals* (1.08 g, 75%); m.p. 277 °C (from hexanes–ethyl acetate); ν_{max}(KBr)/cm^{-1} 3372 and 3356 (NH), 1605, 1583 and 1506 (C=C), 1526 and 1310 (N=O); δ_H(200 MHz; $CDCl_3$) 0.97 (6 H, s, 3-Me_2), 1.08 and 1.36 (6 H, s, 9-Me_2), 1.10–1.90 (7 H, m, 1-, 2- and 4-H_2, 9a-H), 3.30 (1 H, ddd, *J* 10.7, 11.2 and 4.1, 4a-H), 4.41 (1 H, s, NH), 6.31 (1 H, d, *J* 8.8, 5-H), 7.85 (1 H, dd, *J* 2.4 and 8.8, 6-H) and 8.14 (1 H, d, *J* 2.4, 8-H); δ_C(50 MHz; $CDCl_3$) 21.7, 26.0, 26.5, 32.1, 33.7, 36.0, 39.9, 47.7, 47.9 and 48.8 (C-1, -2, -3, -4, -4a, -9a, 9 and 3- and 9-Me_2), 112.3, 123.3 and 124.0 (C-5, -6 and -8), 130.1 (C-8a), 137.5 (C-10a) and 148.9 (C-7); *m/z* 288 (M^+, 58%), 273 (M^+ − CH_3, 100), 69 (84) and 55 (58) (Found: M^+, 288, 1838; C, 70.7; H, 8.4; N, 9.8%. $C_{17}H_{24}N_2O_2$ requires M, 288.1841; C, 70.80; H, 8.39; N, 9.71%).

Methyl trans-3,3,9,9-*tetramethyl*-1,2,3,4,4a,9,9a,10-*octahydroacridine*-7-*carboxylate* **15**. Obtained by flash chromatography [light petroleum–ether acetate (50:1, then 15:1)] as *crystals* (1.36, g, 90%); m.p. 212 °C (from hexanes–ethyl acetate); ν_{max}(KBr)/cm^{-1} 3358 and 3340 (NH), 1707 (CO_2Me), 1604 and 1517 (C=C); δ_H(200 MHz; $CDCl_3$) 0.92 (6 H, s, 3-Me_2), 1.05 and 1.31 (6 H, s, 9-Me_2), 1.10–1.80 (7 H, m, 1-, 2- and 4-H_2, 9a-H), 3.20 (1 H, ddd, *J* 11.0, 10.4 and 4.0, 4a-H), 3.79 (3 H, s, CO_2Me), 4.23 (1 H, s, NH), 6.32 (1 H, d, *J* 8.4, 5-H), 7.59 (1 H, dd, *J* 2.0 and 8.4, 6-H) and 7.90 (1 H, d, *J* 2.0, 8-H); δ_C(50 MHz; $CDCl_3$) 20.6, 24.8, 25.8, 26.3, 30.7, 32.7, 34.5, 38.9, 46.8, 47.1 and 51.1 (C-1, -2, -3, -4, -9 and 3- and 9-Me_2), 112.5, 116.8, 128.2, 128.6 and 129.6 (C-5, -6, -10a, -8 and 8a), 147.3 (C-7) and 167.4 (CO_2Me); *m/z* 301 (M^+, 82%), 286 ($M^+ + 1 - CH_3$, 100), 270 (35), 254 (30), 216 (82), 84 (97), 69 (88) and 57 (91) (Found: M^+, 301.2038; C, 75.8; H, 9.15; N, 4.7%. $C_{19}H_{27}NO_2$ requires M, 301.2041; C, 75.71; H, 9.03; N, 4.65%).

trans-3,3,9,9-*Tetramethyl*-7-*trifluoromethyl*-1,2,3,4,4a,9,9a,10-*octahydroacridine* **16**. Obtained by flash chromatography [light petroleum–ethyl acetate (100:1)] as *crystals* (1.38 g,

89%); m.p. 209 °C (from hexanes–ethyl acetate); ν_{max}(KBr)/cm^{-1} 3428 and 3406 (NH), 1615 and 1520 (C=C), 1365, 1325 and 1260 (C–F) and 814 (1,3,4-trisubstituted aryl); δ_H(200 MHz; $CDCl_3$) 0.86 (6 H, s, 3-Me_2), 0.78 and 1.06 (6 H, s, 9-Me_2), 0.85–1.78 (7 H, m, 1-, 2- and 4-H_2, 9a-H), 3.28 (1 H, ddd, *J* 10.9, 10.6 and 4.2, 4a-H), 3.89 (1 H, s, NH), 6.03 (1 H, d, *J* 8.0, 5-H), 7.20 (1 H, dd, *J* 1.5 and 8.0, 6-H) and 7.47 (1 H, d, *J* 1.5, 8-H); δ_C(50 MHz; $CDCl_3$) 20.8, 25.0, 26.1, 26.7, 31.7, 32.9, 34.9, 39.2 and 47.3 (C-1, -2, -3, -4, -4a, -9a, -9 and 3- and 9-Me_2) and 112.9, 123.4, 123.6, 123.7, 130.5 and 145.8 (C-5, -6, -8-, -8a, -10a and -7); *m/z* 311 (M^+, 80%), 296 ($M^+ + 1 - CH_3$, 100), 225 (96), 206 (84), 69 (100), 67 (91) and 55 (98) (Found: M^+, 311.1852; C, 69.4; H, 7.8; N, 4.55%. $C_{18}H_{24}NF_3$ requires M, 311.1860; C, 69.43; H, 7.77; N, 4.50%).

2-*Isopropenyl*-5,5-*dimethyl*-N-(4′-*nitrophenyl*)*cyclohexylamine* **18**. *Yellow crystals* (115 mg, 8%); m.p. 159 °C (from hexanes–ethyl acetate); ν_{max}(KBr)/cm^{-1} 3362 (N–H), 1598 and 1505 (C=C), 1528 and 1308 (N=O) and 832 (1,4-disubstituted aryl); δ_H(200 MHz; $CDCl_3$) 0.94 and 1.07 (6 H, s, 5-Me_2), 1.59 (3 H, s, C*Me*=CH_2), 0.92–2.07 (7 H, m, 2-H and 3-, 4-and 6-H_2), 3.44 (1 H, ddd, *J* 3.8, 10.6 and 10.4, 1-H), 4.21 (1 H, s, NH), 4.78 (2 H, m, =CH_2), 6.42 (2 H, d, *J* 9.4, 2′- and 6′-H) and 8.02 (2 H, d, *J* 9.4, 3′- and 5′-H); δ_C(50 MHz; $CDCl_3$) 18.0, 21.9, 31.1, 31.4, 34.2, 40.9, 52.0, 53.0 and 58.5 (C-1, -2, -3, -4, -5, -6, C*Me*=CH_2 and 5-Me_2), 112.8 (=CH_2), 110.8, 126.4, 137.1 and 152.8 (C-1′, -2′, -3′, -4′, -5′ and -6′), 146.5 (*C*Me=CH_2); *m/z* 288 (M^+, 38%), 273 ($M^+ - CH_3$, 31), 272 (30), 258 [$M^+ - (CH_3)_2$, 28], 205 (100), 164 (60), 57 (51) and 55 (52) (Found: M^+, 288.1837; C, 70.25; H, 8.6; N, 9.8%. $C_{17}H_{24}N_2O_2$ requires M, 288.1841; C, 70.80; H, 8.39; N, 9.71%).

Methyl 4-(2-*isopropenyl*-5,5-*dimethylcyclohexylamino*)*benzoate* **19**. *Crystals* (90 mg, 6%); m.p. 143 °C (from hexanes–ethyl acetate); ν_{max}(KBr)/cm^{-1} 3399 and 3368 (N–H), 3070 (C=CH_2), 1707 (CO_2Me) and 1604, 1578 and 1525 (C=C); δ_H(200 MHz; $CDCl_3$) 0.91 and 1.04 (6 H, s, 5-Me_2), 1.54 (3 H, s, C*Me*=CH_2), 0.87–2.00 (7 H, m, 2-H and 3-, 4-, 6-H_2), 3.39 (1 H, ddd, *J* 3.7, 11.1 and 10.8, 1-H), 3.79 (3 H, s, CO_2Me), 3.97 (1 H, s, NH), 4.75 (2 H, m, CMe=C*H*$_2$), 6.45 (2 H, d, *J* 6.9, 3′- and 5′-H) and 7.80 (2 H, d, *J* 6.9, 2′- and 6′-H); δ_C(50 MHz; $CDCl_3$) 18.0, 24.4, 27.7, 31.5, 32.6, 38.4, 45.3, 49.4, 51.2 and 52.6 (C-1, -2, -3, -4, -5, -6, -9, OMe and 5-Me_2), 111.1 (C-4′), 112.4 (=CH_2), 117.3 (C-2′ and -6′), 131.4 (C-3′ and -5′), 146.9 (*C*Me=CH_2), 151.3 (C-1′) and 167.1 (*C*O_2Me); *m/z* 301 (M^+, 24%), 286 ($M^+ + 1 - CH_3$, 18), 270 (15), 245 (17), 218 (100), 177 (48), 164 (23), 151 (23), 91 (22), 79 (22), 69 (24) and 55 (27) (Found: M^+, 301.2039; C, 75.6; H, 9.0; N, 4.8%. $C_{19}H_{27}NO_2$ requires M, 301.2042. C, 75.71; H, 9.03; N, 4.65%).

2-*Isopropenyl*-5,5-N-(4′-*trifluoromethylphenyl*)*cyclohexylamine* **20**. *Crystals* (93 mg, 6%); m.p. 144 °C (from hexanes–ethyl acetate); ν_{max}(KBr)/cm^{-1} 3419 and 3411 (N–H), 3073 (C=CH_2), 1643 (NH), 1615 and 1530 (C=C), 1322 and 1294 (C–F) and 822 (1,4-disubstituted aryl); δ_H(200 MHz; $CDCl_3$) 0.94 and 1.07 (6 H, s, 5-Me_2), 1.61 (3 H, s, C*Me*=CH_2), 0.90–2.03 (7 H, m, 2-H and 3-, 4- and 6-H_2), 3.38 (1 H, ddd, *J* 3.8, 10.6 and 10.4, 1-H), 3.74 (1 H, s, NH), 4.79 (2 H, m, =CH_2), 6.51 (2 H, d, *J* 8.3, 2′- and 6′-H) and 7.35 (2 H, d, *J* 8.3, 3′- and 5′-H); δ_C(50 MHz; $CDCl_3$) 18.1, 24.5, 27.8, 31.7, 32.8, 38.6, 45.5, 49.7 and 52.9 (C-1, -2, -3, -4, -5, -6 and 5-Me_2), 112.6 (C-8), 111.6, 126.5 and 126.6 (C-1′, -2′, -3′, -5′ and -6′), 147.2 (C-7) and 150.1 (C-4′); *m/z* 311 (M^+, 50%), 292 ($M^+ - F$, 18), 254 ($M^+ - 3F$, 18), 228 (100), 187 (68), 69 (52), 68 (59), 67 (62) and 55 (53) (Found: M^+, 311.1851; C, 69.6; H, 7.8; N, 4.55%. $C_{18}H_{24}F_3N$ requires M, 311.1860; C, 69.43; H, 7.77; N, 4.50%).

trans-*Bis*(6,6,9,9-*tetramethyl*-5,6,7,8,8a,9,10,10a-*octahydroacridin*-2-*yl*)*methane* **33**. *Pale yellow crystals* (710 mg, 57%); m.p. 248 °C (from hexanes–ethyl acetate); ν_{max}(KBr)/cm^{-1} 1624 and 1500 (C=C), 1317 (C–N) and 806 (1,3,4-trisubstituted aryl); δ_H(200 MHz; $CDCl_3$) 0.96 (12 H, s, 9-Me_2), 1.11 and 1.29 (12 H, s, 6-Me_2), 0.91–1.89 (14 H, m, 5-, 7- and 8-H_2 and 8a-H), 3.19 (2 H, ddd, *J* 10.8, 10.8 and 4.5, 10a-H), 3.72–3.77 (3 H, m, NH and CH_2), 6.36 (2 H, d, *J* 7.9, 4-H), 6.74 (2 H, dd, *J* 1.9 and 7.9, 3-H) and 7.04 (2 H, d, *J* 1.9, 1-H); δ_C(50 MHz; $CDCl_3$) 20.9, 24.1, 27.0, 27.4, 30.3, 33.0, 34.9, 38.8, 47.3 and 48.1 (C-5, -6, -7, -8, -8a, -9, -10a, and 6- and 9-Me_2), 114.0, 126.9 and 127.1 (C-1, -3 and -4), 130.4 and 131.3 (C-2, -9a) and 141.1 (C-4a); *m/z* 498 (M^+, 57%), 483 ($M^+ - CH_3$, 52), 441 (45), 427 (40), 71 (84) and 57 (100) (Found: M^+, 498.3973; C, 84.5; H, 9.9; N, 5.7%. $C_{35}H_{50}N_2$ requires M, 498.3990; C, 84.28; H, 10.10; N, 5.62%).

trans-*Bis*(6,6,9,9-*tetramethyl*)-5,6,7,8,8a,9,10,10a-*octahydroacridin*-2-*yl*) *ether* **34**. *Pale brown crystals* (850 mg, 68%); m.p. 137 °C (from hexanes–ethyl acetate); ν_{max}(KBr)/cm^{-1} 3384 and 3376 (N–H), 1493 (C=C), 1264 (C–O) and 808 (1,3,4-trisubstituted aryl); δ_H(200 MHz; $CDCl_3$) 0.94 (12 H, s, 6-Me_2), 1.13 and 1.24 (12 H, s, 9-Me_2), 0.87–1.80 (14 H, m, 5-, 7- and 8-H_2 and 8a-H), 3.17 (2 H, ddd, *J* 3.8 and 10.5 and 10.5, 10a-H), 3.40 (2 H, s, NH), 6.36 (2 H, d, *J* 8.6, 4-H), 6.58 (2 H, dd, *J* 2.6 and 8.6, 3-H) and 6.89 (2 H, d, *J* 2.6, 1-H); δ_C(50 MHz; $CDCl_3$) 21.0, 25.0, 27.0, 27.3, 31.0, 35.2, 39.2, 47.2, 47.4 and 47.8 (C-5, -6, -7, -8, -8a, -9, -10a and 6- and 9-Me_2), 114.8, 116.8 and 117.0 (C-1, -3 and -4), 132.9 and 138.4 (C-4a, -9a), and 149.7 (C-2); *m/z* 500 (M^+, 84%), 485 ($M^+ - CH_3$, 68), 467 (56), 447 (58), 258 (72), 71 (90), 69 (87), 57 (96) and 55 (100) (Found: M^+, 500.3767; C, 81.7; H, 10.0; N, 5.2%. $C_{34}H_{48}N_2O$ requires M, 500.3787; C, 81.55; H, 9.66; N, 5.59%).

trans-*Bis*(6,6,9,9-*tetramethyl*-5,6,7,8,8a,9,10,10-*octahydroacridin*-2-*yl*) *sulfone* **35**. *Pale brown solid* (795 mg, 58%); m.p. 192 °C (from hexanes–ethyl acetate); ν_{max}(KBr)/cm^{-1} 3374 and 3359 (N–H), 1597 and 1512 (C=C), 1331 and 1152 (SO_2), 1079 (S–O) and 817 (1,3,4-trisubstituted aryl); δ_H(200 MHz; $CDCl_3$) 0.93 (12 H, s, 6-Me_2), 1.03 and 1.29 (12 H, s, 9-Me_2), 0.84–1.18 (14 H, m, 5-, 7- and 8-H_2 and 8a-H), 3.21 (2 H, ddd, *J* 4.0, 10.7 and 11.0, 10a-H), 3.99 (2 H, s, NH), 6.32 (2 H, d, *J* 8.6, 4-H), 7.36 (2 H, dd, *J* 2.2 and 8.6, 3-H) and 7.72 (2 H, d, *J* 2.2, 1-H); δ_C(50 MHz; $CDCl_3$) 20.8, 25.9, 26.4, 31.0, 32.8, 35.1, 39.2, 47.1, 47.2 and 47.4 (C-5, -6, -7, -8, -8a, -9, -10a and 6- and 9-Me_2), 113.0, 125.8 and 126.2 (C-1, -3 and -4), 129.4 and 130.5 (C-4a and C-9a) and 146.6 (C-2); *m/z* 548 (M^+, 96%), 259 (75), 109 (79), 69 (84), 57 (91) and 55 (100) (Found: M^+, 548.3436; C, 74.2; H, 9.2; N, 4.8%. $C_{34}H_{48}N_2O_2S$ requires M, 548.3419; C, 74.41; H, 8.82; N, 5.10%).

trans-6,6,9,9-*Tetramethyl*-5,6,7,8,8a,9,10,10a-*octahydroacridine*-2-*amine* **21**.—A solution of nitro compound **14** (288 mg, 1.00 mmol) and hydrazine hydrate (2.50 mmol) in ethanol (10 cm^3) was warmed to 40 °C and treated with Raney-Ni in small portions until the evolution of hydrogen had ceased. Then the mixture was refluxed for 30 min. After cooling to room temperature, the mixture was filtered, the residue was washed with ethanol, and the filtrate was evaporated to yield the *amine* **21** as a brown solid (255 mg, 99%); m.p. 298 °C (from EtOH); ν_{max}(KBr)/cm^{-1} 3347 and 3335 (N–H), 1611 and 1506 (C=C) and 807 and 682 (1,3,4-trisubstituted aryl); δ_H(200 MHz; $CDCl_3$) 0.90 (6 H, s, 6-Me_2), 1.07 and 1.23 (6 H, s, 9-Me_2), 0.81–1.73 (7 H, m, 5-, 7- and 8-H_2 and 8a-H), 3.07–3.30 (4 H, m, NH_2, NH, 10a-H), 6.27 (1 H, d, *J* 8.2, 4-H), 6.36 (1 H, dd, *J* 8.2 and 2.3, 3-H) and 6.59 (1 H, d, *J* 2.3, 1-H); δ_C(50 MHz; $CDCl_3$) 21.0, 25.1, 27.2, 27.5, 30.9, 33.0, 35.0, 39.3, 47.4 and 48.2 (C-5, -6, -7, -8, -8a, -9, -10a and 6- and 9-Me_2), 114.7, 115.0 and 115.3 (C-1, -3 and -4) and 133.0, 136.4 and 137.1 (C-2, -4a and -9a); *m/z* 258 (M^+, 68%), 243 ($M^+ - CH_3$, 82), 71 (66), 69 (62), 60 (84) and 57 (100) (Found: M^+, 258.2095. $C_{17}H_{26}N_2$ requires M, 258.2091).

General Procedure for the Lewis Acid-Catalysed Cyclization.—To a cooled solution of an imine (1.00 mmol) in dichloromethane (20 cm^3) was added dropwise $MeAlCl_2$ (2.5

mmol; 1.0 mol dm^{-1} solution in hexane) at −78 °C over a period of 30 min. The cooling was removed and the mixture was stirred for 2 days at room temperature. Then the reaction mixture was poured into ice-cold 2 mol dm^{-3} NaOH (50 cm^3) and the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 50 cm^3) and the combined organic layers were dried over sodium sulfate and evaporated. The crude products were purified by flash chromatography on SiO_2 or preparative HPLC.

trans,trans-3,3,7,7,10,10,14,14-*Octamethyl*-1,2,3,4,4a,5,7,7a,8,9,10,11,11a,12,14,14a-*hexadecahydroquino*[2,3-b]*acridine* **23**. Work-up yielded a red solid as crude product (388 mg, 95%), which contained a mixture of compounds **23** and **44** (52.6:47.4, determined by analytical HPLC). Separation by preparative HPLC gave *title compound* **23** as a red solid; m.p. 208–210 °C (decomp.); ν_{max}(KBr)/cm^{-1} 3375 (N–H), 3016 (C–H, aryl), 1509 (C=C) and 911; δ_H(200 MHz; C_6D_6) 0.80–1.80 (16 H, m, 1-, 2-, 4-, 8-, 9-, 11-H_2, 7a-, 14a-H and 2 × NH), 0.93 (12 H, s, 3- and 10-Me_2), 1.17 (3 H, s), 1.18 (3 H, s), 1.24 (3 H, s) and 1.26 (3 H, s) (together 7- and 14-Me_2), 3.12 (2 H, ddd, *J* 10.6, 10.0 and 4.2, 4a-H, 11a-H) and 6.38 (2 H, s, 6- and 13-H); δ_C(50 MHz; C_6D_6) 21.0, 25.0, 27.4, 27.6, 30.8, 33.0, 34.7, 39.2, 47.4 and 48.3 (C-1, -2, -3, -4, -4a, -7, -7a, -8, -9, -10, -11, -11a, -14 and -14a), 113.0 (C-6 and -13) and 131.4 and 135.2 (C-5a, -6a, -12a and -13a); *m/z* 408 (M^+, 100%), 391 ($M^+ - CH_3$, 84), 69 (55) and 55 (26) (Found: M^+, 408.3495; C, 82.0; H, 10.7; N, 6.7%. $C_{28}H_{44}N_2$ requires M, 408.3504; C, 82.29; H, 10.85; N, 6.85%).

trans,trans-3,3,7,7,10,10,14,14-*Octamethyl*-1,2,3,4,4a,7,7a,8,9,10,11,11a,14,14a-*tetradecahydroquino*[2,3-b]*acridine* **44**. *Yellow solid*; ν_{max}(KBr)/cm^{-1} 1582 and 1511 (C=C); δ_H(200 MHz; C_6D_6) 0.80–1.40 (12 H, 1-, 2-, 4-, 8-, 9- and 11-H_2), 0.82 (6 H, s, 3- and 10-Me), 0.90 (6 H, s, 3- and 10-Me), 0.95 (6 H, s, 7- and 14-Me), 0.99 (6 H, s, 7- and 14-Me), 2.40 (2 H, ddd, *J* 12.9, 3.4 and 2.6, 7a- and 14a-H), 3.55 (2 H, 't', *J* 12.0, 4a- and 11a-H) and 6.93 (2H, s, 6- and 13-H); δ_C(50 MHz; C_6D_6) 21.3, 23.1, 23.9, 24.9, 31.8, 33.2, 34.5, 39.5, 48.5, 48.7 and 57.4 (C-1, -2, -3, -4, -4a, -7, -7a, -8, -9, -10, -11, -11a, -14 and -14a), 129.8 (C-6 and -13), 142.4 (C-6a and -13a) and 158.6 (C-5 and -12a); *m/z* 406 (M^+, 38%), 391 ($M^+ - CH_3$, 35), 248 (41), 192 (51), 149 (58), 91 (100) and 57 (93) (Found: M^+, 406.3346. $C_{28}H_{42}N_2$ requires M, 406.3348).

trans,trans-3,3,8,8,11,11,16,16-*Octamethyl*-1,2,3,4,4a,5,8,8a,9,10,11,12,12a,13,16,16a-*hexadecahydroacridino*[4,3-c]*acridine* **45**. Red solid as a crude product (417 mg, 91%), which contained 75% main product and 20% of two unidentified by-products (determined by HPLC) and was further purified by preparative HPLC to yield *red crystals*; m.p. 216 °C (from hexanes–ethyl acetate–triethylamine); ν_{max}(KBr)/cm^{-1} 3367 (N–H) and 1515 (C=C); δ_H(200 MHz; $CDCl_3$) 0.80–1.80 (14 H, m, 1-, 2-, 4-, 9-, 10- and 12-H_2 and 8a- and 16a-H), 1.03 (12 H, s, 3- and 11-Me_2), 1.17 (6 H, s, 8- and 16-Me), 1.34 (6 H, s, 8- and 16-Me), 2.56 (2 H, ddd, *J* 10.6, 10.4 and 4.3, 4a- and 12a-H), 3.20–3.60 (2 H, br s, NH), 7.00 (2 H, d, *J* 8.8, 6- and 14-H) and 7.30 (2 H, d, *J* 8.8, 7- and 15-H); δ_C(50 MHz; $CDCl_3$) 21.0, 25.1, 27.1, 27.2, 31.1, 33.1, 34.9, 39.3, 45.6, 47.3 and 47.8 (C-1, -2, -3, -4, -4a, -8, -8a, -9, -10, -11, -12, -12a and 3-, 8-, 11- and 16-Me_2), 108.3 (C-6 and -14), 121.3 (C-7a and -15a), 124.7 (C-5b and -13b), 127.5 (C-7 and -15) and 137.8 (C-5a and -13a); *m/z* 458 (M^+, 100%), 443 ($M^+ - CH_3$, 50) and 69 (70) (Found: M^+, 458.3652; C, 83,75; H, 10.1; N, 6.0%. $C_{32}H_{46}N_2$ requires M, 458.3660; C, 83.79; H, 10.11; N, 6.11%).

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